

STATEMENT

I, Yukio KAWAHARA—of ARK Mori Building, 13F, 12-32, Akasaka 1-chome, Minato-ku, Tokyo 107-6013 Japan—hereby declare that I am conversant in both Japanese and English and that I believe the following is true and correct translation of Japanese Patent Application No. 11-172405.

Date: May 18, 2004



Yukio KAWAHARA

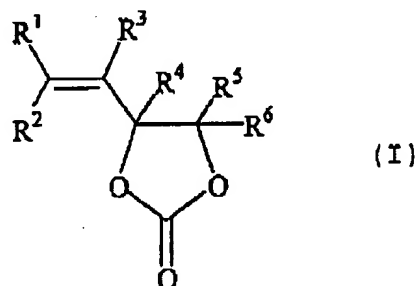
[Designation of Document] Specification

[Title of the Invention] Non-aqueous electrolyte
secondary battery

[Claims]

1. A non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, characterized in that said non-aqueous solvent contains a vinylene carbonate compound represented by the following general formula (I) in an amount of from 0.01% to 20% by weight:

[Ka 1]



wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. The non-aqueous electrolyte secondary battery according to Claim 1, characterized in that said negative electrode contains a carbon-based material capable of absorbing and releasing lithium.

3. The non-aqueous electrolyte secondary battery according to Claim 1 or 2, characterized in that said

non-aqueous solvent is a mixed solvent containing a cyclic carbonate selected from the group consisting of alkylene carbonates the alkylene group moiety of which each have from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonates the alkyl group moiety of which each have from 1 to 4 carbon atoms except the vinylethylene carbonate compound of the general formula (I) each in an amount of not smaller than 20 vol-%, with the proviso that the content of said carbonates accounts for not smaller than 70 vol-% based on the total amount thereof.

4. The non-aqueous electrolyte secondary battery according to any one of Claims 1 to 3, characterized in that said carbon-based material capable of absorbing and releasing lithium comprises a carbon-based material having a d value of from 0.335 to 0.34 nm on lattice plane (002 plane) as determined by X-ray diffractometry.

5. The non-aqueous electrolyte secondary battery according to any one of Claims 1 to 4, characterized in that said lithium salt is at least one salt selected from LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a non-aqueous electrolyte secondary battery. More particularly, the present invention relates to a non-aqueous electrolyte secondary battery comprising an electrolyte containing a specific vinylethylene carbonate compound. The battery of the invention is subject to minimized decomposition of the electrolyte and exhibits a high capacity as well as excellent storage properties and cycle life performance at high temperatures.

[0002]

[Prior Art]

With the recent trend for the reduction of weight and size of electrical appliances, the development of lithium secondary battery having a high energy density has been being conducted.

Further, with the expansion of the field to which the lithium Secondary battery can be applied, it has been desired to further improve the battery performance.

Extensive studies have been heretofore made of secondary battery comprising metallic lithium as a negative electrode as battery which can attain a high capacity. However, the greatest technical problem that prevents the practical use of such a secondary battery was that when charge and discharge are repeated, metallic lithium grows in the form of dendrite and eventually

reaches the positive electrode, causing shortcircuiting in the battery.

To cope with this problem, a non-aqueous electrolyte secondary battery comprising as a negative electrode a carbon-based material capable of absorbing/releasing lithium ion such as coke, artificial graphite and natural graphite has been proposed. In such a non-aqueous electrolyte secondary battery, lithium doesn't exist in metallic state, making it possible to inhibit the formation of dendrite and improve the battery life and safety.

[0003]

In particular, a graphite-based carbon material such as artificial graphite and natural graphite is expected as a material which can improve an energy density per unit volume.

However, in a non-aqueous electrolyte secondary battery comprising as a negative electrode various graphite-based electrode materials, singly or in admixture with other negative electrode materials capable of absorbing and releasing lithium, if an electrolyte comprising as a main solvent propylene carbonate which is normally and preferably used in a lithium primary battery is used, the decomposition reaction of the solvent proceeds violently on the surface of the graphite

electrode, disabling the smooth absorption of lithium into the graphite electrode and smooth release of lithium from the graphite electrode.

On the other hand, ethylene carbonate undergoes little such decomposition and thus has been widely used as a main solvent of an electrolyte for a non-aqueous electrolyte secondary battery. However, even if ethylene carbonate is used as a main solvent, the electrolyte decomposes on the surface of the electrode during charge and discharge, raising problems of drop of charge and discharge efficiency, deterioration of cycle performance, etc.

[0004]

Under these circumstances, Japanese Patent Laid-Open No. 1992-87156 proposes, in a non-aqueous electrolyte battery comprising as a negative electrode lithium, an electrolyte comprising as a solvent a compound of which chain has unsaturated carbon-carbon bond difficultly reactive with lithium, e.g., vinyl ethylene carbonate. Japanese Patent Laid-Open No. 1996-45545 proposes, in a lithium battery comprising a graphite negative electrode, an electrolyte comprising vinyl ethylene carbonate and a derivative thereof for suppressing the decomposition of the electrolyte.

[0005]

[Problems that the Invention is to Solve]

However, the electrolytes disclosed in the above cited publications leave something to be desired, though showing an excellent effect in its own way.

The present invention has been worked out to solve these problems. An object of the present invention is to provide a non-aqueous electrolyte secondary battery having a high energy density comprising a negative electrode containing a carbon-based material which is subject to minimized decomposition of the electrolyte to exhibit a high charge and discharge efficiency and show excellent storage properties and cycle life performance even at high temperatures.

[0006]

[Means for Solving the Problems]

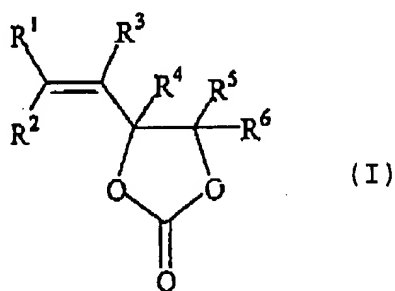
Under these circumstances, the inventors made extensive studies. As a result, it was found that the use of an electrolyte containing a specific vinylethylene carbonate compound as an electrolyte for a non-aqueous electrolyte secondary battery comprising a negative electrode comprising a carbon-based material allows the efficient production of a stable lithium ion-permeable film on the surface of the negative electrode from the beginning of initial charge, making it possible to inhibit excessive decomposition of the electrolyte and hence

improve the charge and discharge efficiency, storage properties and cycle life performance. The present invention has thus been worked out.

In other words, the essence of the invention lies in a non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, characterized in that the foregoing non-aqueous solvent contains a vinyl ethylene carbonate compound represented by the following general formula (I) in an amount of from 0.01% to 20% by weight:

[0007]

[Ka 2]



[0008]

wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

[0009]

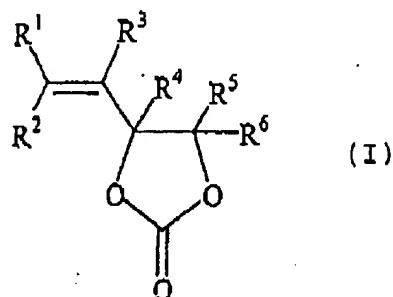
[0010]

[Mode for Carrying Out the Invention]

The non-aqueous electrolyte secondary battery of the present invention is characterized in that the non-aqueous solvent used therein contains a vinyl ethylene carbonate compound represented by the following general formula (I):

[0011]

[Ka 3]



[0012]

wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

[0013]

When R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are alkyl groups having 1 to 4 carbon atoms in the formula (I), specific examples thereof include methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, sec-butyl group, and tert-butyl group. Preferred among these alkyl groups are methyl group and ethyl group. Specific examples of the vinyl ethylene carbonate compound represented by the

general formula (I) include

4-ethenyl-1,3-dioxolane-2-one (occasionally referred to as "vinylethylene carbonate"),

4-ethenyl-4-methyl-1,3-dioxolane-2-one,

4-ethenyl-4-ethyl-1,3-dioxolane-2-one,

4-ethenyl-4-n-propyl-1,3-dioxolane-2-one,

4-ethenyl-5-methyl-1,3-dioxolane-2-one,

4-ethenyl-5-ethyl-1,3-dioxolane-2-one,

4-ethenyl-5-n-propyl-1,3-dioxolane-2-one, etc.

In particular, vinylethylene carbonate, 4-ethenyl-4-methyl-1,3-dioxolane-2-one are preferred, and vinylethylene carbonate is particularly preferred.

[0014]

The compound of the general formula (I) may have substituents so far as the desired effect of the present invention cannot be excessively impaired.

The content of the compound of the general formula (I) in the non-aqueous solvent is normally from 0.01 to 20% by weight, preferably from 0.01 to 10% by weight, more preferably from 0.1 to 5% by weight. When the content of the compound of the general formula (I) falls below 0.01% by weight, the formation of the protective film cannot be sufficiently effected. On the contrary, when the content of the compound of the general formula (I) exceeds 20% by weight, the electrolyte has a high viscosity

and hence a low electrical conductivity, deteriorating the performance of the battery.

[0015]

Examples of the non-aqueous solvent other than the compound of the general formula (I) to be used in the present invention include cyclic carbonates such as ethylene carbonate, propylene carbonate and butylene carbonate, chain carbonates such as dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate, cyclic esters such as γ -butyrolactone and γ -valerolactone, chain esters such as methyl acetate and methyl propionate, cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran and tetrahydropyran, chain ethers such as dimethoxyethane and dimethoxymethane, sulfur-containing organic solvents such as sulfolane and diethylsulfolane, etc. Two or more of these solvents may be used in admixture.

The non-aqueous solvent is preferably a mixed solvent containing a cyclic carbonate selected from the group consisting of alkylene carbonates the alkylene group moiety of which each have from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonates the alkyl group moiety of which each have from 1 to 4 carbon atoms except the vinyl ethylene carbonate compound of the general formula (I) each in

an amount of not smaller than 20 vol-%, with the proviso that the content of the carbonates accounts for not smaller than 70 vol-% based on the total amount thereof.

[0016]

The term "vol-%" as used herein is meant to indicate one measured at room temperature, i.e., 25°C. However, any solvent which stays solid at 25°C shall be heated to its melting point where it is then measured in molten state.

Specific examples of the alkylene carbonate the alkylene group moiety of which has from 2 to 4 carbon atoms include ethylene carbonate, propylene carbonate, butylene carbonate, etc. Preferred among these alkylene carbonates are ethylene carbonate and propylene carbonate.

[0017]

Specific examples of the dialkyl carbonate the alkyl group moiety of which has from 1 to 4 carbon atoms include dimethyl carbonate, diethyl carbonate, di-n-propyl carbonate, ethylmethyl carbonate, methyl-n-propyl carbonate, ethyl-n-propyl carbonate, etc. Preferred among these dialkyl carbonates are dimethyl carbonate, diethyl carbonate, and ethylmethyl carbonate. The mixed non-aqueous solvent may contain solvents other than carbonate.

[0018]

As the solute of the electrolyte to be used in the invention there may be used a lithium salt. The usable lithium salt is not specifically limited so far as it can be used as a solute of an electrolyte. For example, an inorganic lithium salt selected from LiClO_4 , LiPF_6 and LiBF_4 or a fluorine-containing organic lithium salt such as LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ can be used. Preferred among these lithium salts are LiPF_6 and LiBF_4 . Two or more of these lithium salts may be used in admixture.

The molar concentration of a lithium salt as a solute in the electrolyte is normally from 0.5 to 2.0 mols/l. When the molar concentration of the lithium salt falls below 0.5 mols/l or exceeds 2.0 mols/l, it is disadvantageous in that the electrolyte exhibits a low electrical conductivity that is liable to cause deterioration of the battery performance.

[0019]

The material of the negative electrode constituting the battery of the present invention is preferably one containing a carbon-based material capable of absorbing and releasing lithium. Specific examples of such a carbon-based material include pyrolysis products of organic materials obtained under various pyrolysis

conditions, artificial graphite, natural graphite, etc. Preferably, artificial graphite produced by high temperature heat treatment of graphitizable pitch obtained from various raw materials, other artificial graphite such as graphitized mesophase globule and graphitized mesophase pitch-based carbon fiber, purified natural graphite or materials obtained by subjecting these graphites to various surface treatment including pitch may be used, but these carbon-based materials preferably have a d value (interlaminar distance) of from 0.335 to 0.34 nm, more preferably from 0.335 to 0.337 nm on lattice plane (002 plane) determined by X-ray diffractometry. These carbon-based materials preferably have an ash content of not greater than 1% by weight, more preferably not greater than 0.5% by weight, most preferably not greater than 0.1% by weight, and a crystalline size (Lc) of not smaller than 30 nm as determined by X-ray diffractometry according to the method of the Japan Society of Promotion of Scientific Research.

[0020]

Further, the crystalline size of the carbon-based materials is more preferably not smaller than 50 nm, particularly preferably not smaller than 100 nm. The median diameter of a carbon-based material is preferably from 1 to 100 μm , more preferably from 3 to 50 μm , further

preferably from 5 to 40 μm , particularly preferably from 7 to 30 μm as determined by laser diffractometry/scattering method. BET process specific surface area of the carbon-based material is preferably from 0.3 to 25.0 m^2/g , more preferably from 0.5 to 20.0 m^2/g , even more preferably from 0.7 to 15.0 m^2/g , particularly preferably from 0.8 to 10.0 m^2/g . An intensity ratio of peak P_A (peak intensity I_A) in the range of from 1,580 to 1,620 cm^{-1} and peak P_B (peak intensity I_B) in the range of from 1,350 to 1,370 cm^{-1} determined by Raman spectroscopy using argon ion laser: $R (= I_B/I_A)$ is preferably 0 to 0.5 and a peak half width is preferably 26 cm^{-1} or less, particularly preferably 25 cm^{-1} or less in the range of from 1,580 to 1,620 cm^{-1} .

[0021]

Further, the carbon-based material may be used by further mixing a negative electrode material capable of absorbing and releasing lithium therewith. Examples of the negative electrode material capable of absorbing and releasing lithium other than the carbon-based material include metal oxide materials such as tin oxide and silicon oxide, metallic lithium, and various lithium alloys. Two or more of these negative electrode materials may be used in admixture.

The process for the production of a negative

electrode from these negative electrode materials is not specifically limited. The negative electrode can be produced, e.g., by optionally adding a binder, a thickening agent, an electrically-conducting material, a solvent, etc. to a negative electrode material to make a slurry, applying the slurry to a current collector substrate, and then drying the coated substrate. Alternatively, the negative electrode material may be rolled as it is to prepare a sheet-like electrode or may be compression-molded to prepare a pelletized electrode.

[0022]

The binder to be used in the production of the electrode is not specifically limited so far as it is a material inert to the solvent to be used in the production of the electrode or the electrolyte. Specific examples of such a material include polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, isoprene rubber, butadiene rubber, etc.

Examples of the thickening agent include carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidized starch, phosphated starch, casein, etc.

Examples of the electrically-conducting material include metallic materials such as copper and nickel, and carbon-based materials such as graphite and carbon

black.

[0023]

As the material of the current collector for a negative electrode there may be used metals such as copper, nickel and stainless steel. Preferred among these metals is a copper foil because it can be easily formed into a thin film and from the Stand point of cost.

As the material of the positive electrode constituting the battery of the present invention there may be used a material capable of absorbing and releasing lithium such as a lithium transition metal composite oxide material, e.g., lithium cobalt oxide, lithium nickel oxide and lithium manganese oxide.

The process for the production of the positive electrode is not specifically limited. The positive electrode can be produced according to the foregoing process for the production of the negative electrode. Referring to the shape of the positive electrode, a binder, an electrically-conducting material, a solvent, etc. may be optionally added to and mixed with the positive electrode material and the resulting mixture is then applied to a current collector substrate to form a sheet electrode or press-molded to form a pelletized electrode.

As the material of the current collector for positive electrode there may be used a metal such as aluminum,

titanium and tantalum or alloy thereof. Particularly preferred among these materials is aluminum or alloy thereof because it has a light weight and thus gives a high energy density.

[0024]

The material and shape of the separator to be used in the battery of the present invention are not specifically limited.

However, the separator is preferably selected from materials which are inert to the electrolyte and have excellent liquid retaining properties. A porous sheet or nonwoven cloth made of a polyolefin such as polyethylene and polypropylene as a raw material is preferably used.

The process for the production of the battery of the present invention having at least a negative electrode, a positive electrode and a non-aqueous electrolyte is not specifically limited but can be properly selected from those commonly employed.

The shape of the battery is not specifically limited. A cylinder type obtained by spirally winding a sheet-like electrode and a separator, a cylinder type having an inside out structure comprising a pelletized electrode and a separator in combination, a coin type having a pelletized electrode and a separator laminated on each other, etc. can be used.

[0025]

[Examples]

The present invention will be further described in the following examples and comparative examples, but the present invention should not be construed as being limited thereto so far as they fall within the scope of the invention.

[0026]

EXAMPLE 1

An electrolyte was prepared by dissolving vinylethylene carbonate in propylene carbonate in an amount of 5% by weight, and then dissolving thoroughly dried lithium hexafluorophosphate (LiPF_6) as a solute in the solution in an amount of 1 mol/l in dried argon atmosphere.

To 94 parts by weight of KS-44 (trade name; produced by Timcal Co., Ltd.), which is an artificial graphite powder having a d value of 0.336 nm on lattice plane (002 plane) as determined by X-ray diffractometry, a crystalline size (L_c) of not lower than 100 nm (264 nm), an ash content of 0.04% by weight, a median diameter of 17 μm as determined by laser diffractometry/scattering method, a BET process specific surface area of 8.9 m^2/g , an intensity ratio of peak P_A (peak intensity I_A) in the range of from 1,580 to 1,620 cm^{-1} and peak P_B (peak intensity

I_B) in the range of from 1,350 to 1,370 cm^{-1} determined by Raman spectroscopy using argon ion laser: $R (= I_B/I_A)$ of 0.15 and a peak half width of 22.2 cm^{-1} in the range of from 1,580 to 1,620 cm^{-1} were added 6 parts by weight (solid content) of a dispersion of styrene-butadiene rubber (SER) in distilled water. The mixture was then stirred by means of a disperser to make a slurry. The slurry thus made was uniformly applied to a copper foil having a thickness of 18 μm as a negative electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare an electrode as a working electrode. A lithium foil was then provided as a counter electrode on the working electrode with a separator impregnated with the electrolyte interposed therebetween to prepare a coin type half cell.

[0027]

COMPARATIVE EXAMPLE 1

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving vinylene carbonate in propylene carbonate in an amount of 5% by weight, and then dissolving LiPF_6 in the solution in an amount of 1 mol/l was used.

COMPARATIVE EXAMPLE 2

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by

dissolving LiPF_6 in propylene carbonate in an amount of 1 mol/l was used.

[0028]

EXAMPLE 2

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving vinylene carbonate in a 1 : 1 (by volume) mixture of ethylene carbonate and diethyl carbonate in an amount of 2% by weight, and then dissolving LiPF_6 in the solution in an amount of 1 mol/l was used.

[0029]

COMPARATIVE EXAMPLE 3

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving LiPF_6 in a 1 : 1 (by volume) mixture of ethylene carbonate and diethyl carbonate in an amount of 1 mol/l was used.

[0030]

Subsequently, the coin type half cells of Examples 1 and 2 and Comparative Examples 1 to 3 thus prepared were subjected to charge discharge test involving discharge with a constant current of 0.2 mA to a termination voltage of 0 V and charge with a constant current of 0.4 mA to a termination voltage of 1.5 V at 25°C.

The half cells of Examples 1 and 2 and Comparative

Example 3 which had been subjected to 10 cycles of charge and discharge were stored in doped state at 60°C for 48 hours, subjected to dedoping, and then examined for storage properties.

The capacity-potential curve developed by charge and discharge at the 1st cycle in Example 1 and Comparative Examples

1 and 2 are shown in Figs. 1, 2 and 3, respectively. The term "capacity" as used herein is meant to indicate the capacity of the graphite used as a working electrode per weight.

The dedoped capacity (capacity of lithium dedoped from the working electrode) at the 1st cycle and the efficiency (dedoped capacity \times 100/doped capacity) in Examples 1 and 2, and Comparative Examples 1 to 3 are set forth in Table 1.

As storage properties, the percentage of capacity of Examples 1 and 2 and Comparative Example 3 before (dedoped capacity at the 10th cycle) and after (dedoped capacity at the 11th cycle) storage are set forth in Table 2.

[0031]

As shown in Fig. 3, in the case of single use of propylene carbonate as a solvent, a flat portion is observed in the vicinity of 0.8 V where the decomposition

of the electrolyte proceeds, disabling doping to 0 V. As shown in Fig. 2, when an electrolyte containing vinylene carbonate is used, doping is made possible to 0 V, but the decomposition of the electrolyte cannot be sufficiently conducted. As shown in Fig. 1, the use of an electrolyte containing a vinyl ethylene carbonate makes it possible to inhibit the excessive decomposition of the electrolyte.

As can be seen in Tables 1 and 2, the use of an electrolyte containing vinyl ethylene carbonate makes it possible to enhance efficiency while keeping a high capacity and improve storage properties at high temperatures.

[0032]

[Table 1]

Table 1

	Dedoped capacity at 1st cycle (mAh/g)	Efficiency at 1st cycle (%)
Example 1	327	91.6
Example 2	324	91.6
Comparative Example 1	315	66.6
Comparative Example 2	-	-
Comparative Example 3	318	91.2

[0033]

[Table 2]

Table 2

	Storage properties (%)
Example 1	97.6
Example 2	97.1
Comparative Example 3	96.7

[0034]

[Effect of the Invention]

In a non-aqueous electrolyte secondary battery comprising a negative electrode containing a carbon-based material, the use of a non-aqueous solvent containing a vinyl ethylene carbonate compound represented by the general formula (I) makes it possible to prepare a battery which is subject to minimized decomposition of the electrolyte and provides a high capacity as well as exhibits excellent storage properties and cycle life performance even at a high temperature and hence contribute to the reduction of the size of and improve the performance of the non-aqueous electrolyte secondary battery.

[Brief Description of the Drawings]

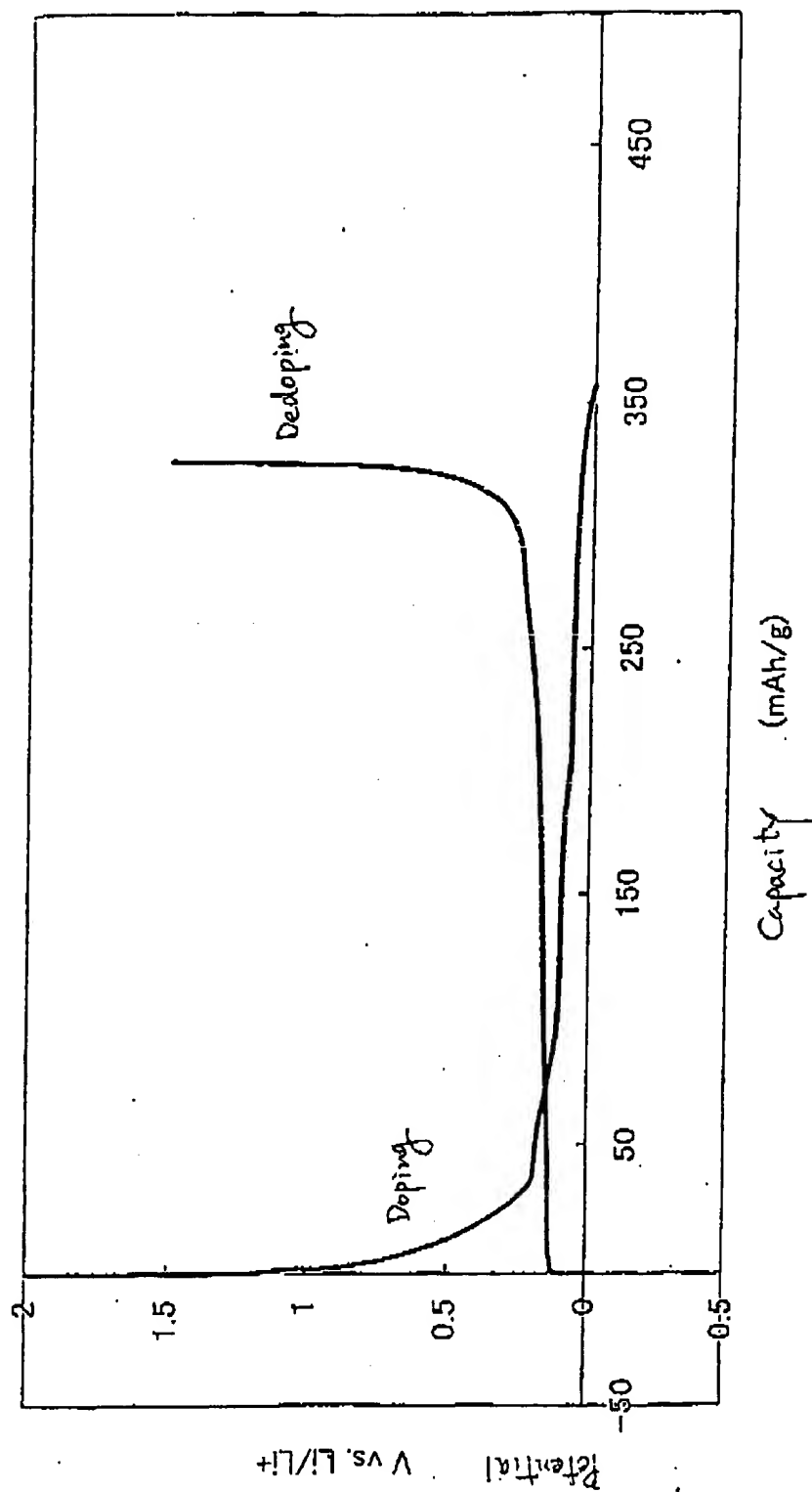
Fig. 1 is a graph illustrating the capacity-potential curve developed by charge and discharge at the 1st cycle in Example 1 of the present

invention.

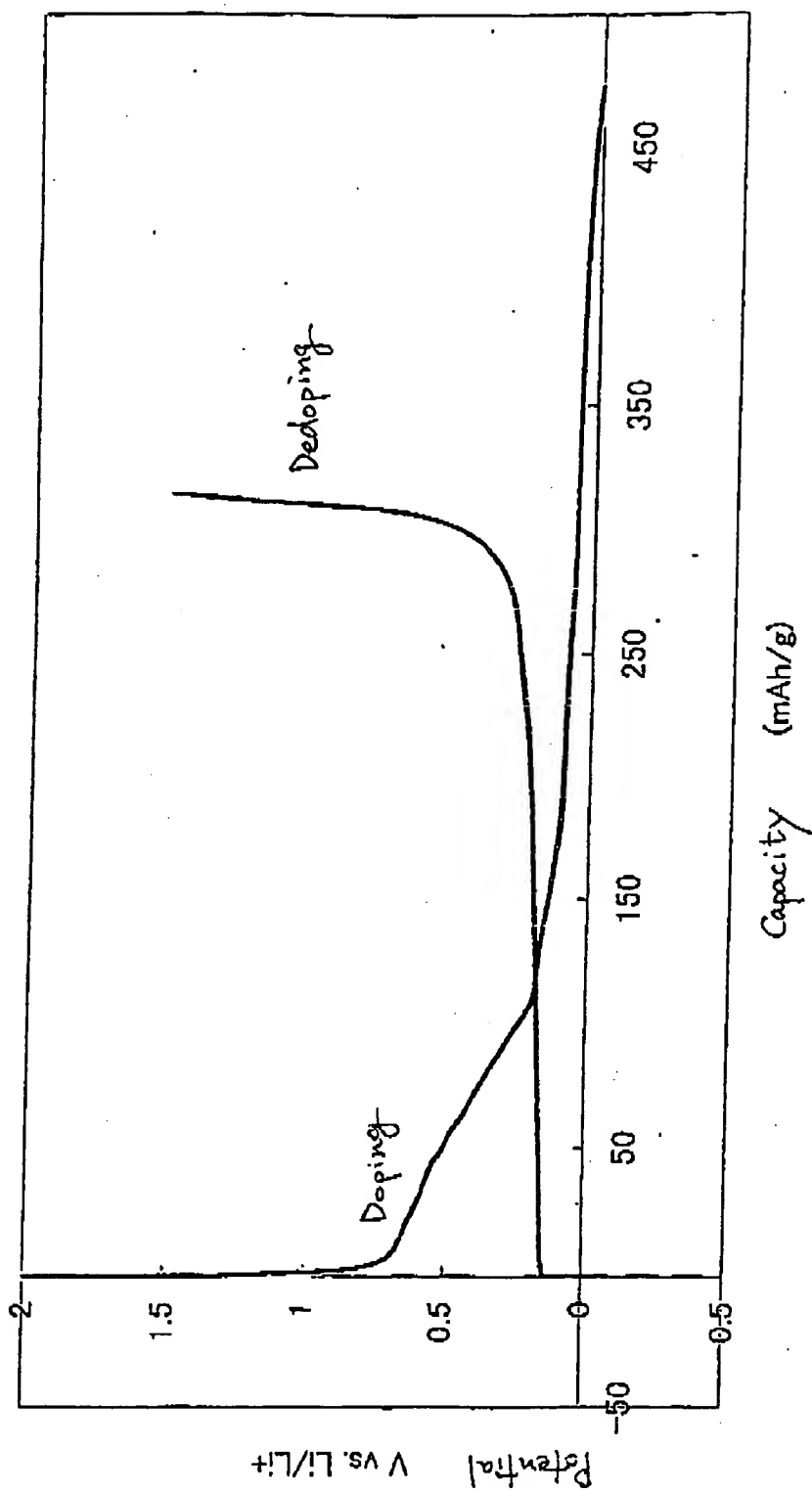
Fig. 2 is a graph illustrating the capacity-potential curve developed by charge and discharge at the 1st cycle in Comparative Example 1 of the present invention.

Fig. 3 is a graph illustrating the capacity-potential curve developed by charge and discharge at the 1st cycle in Comparative Example 2 of the present invention.

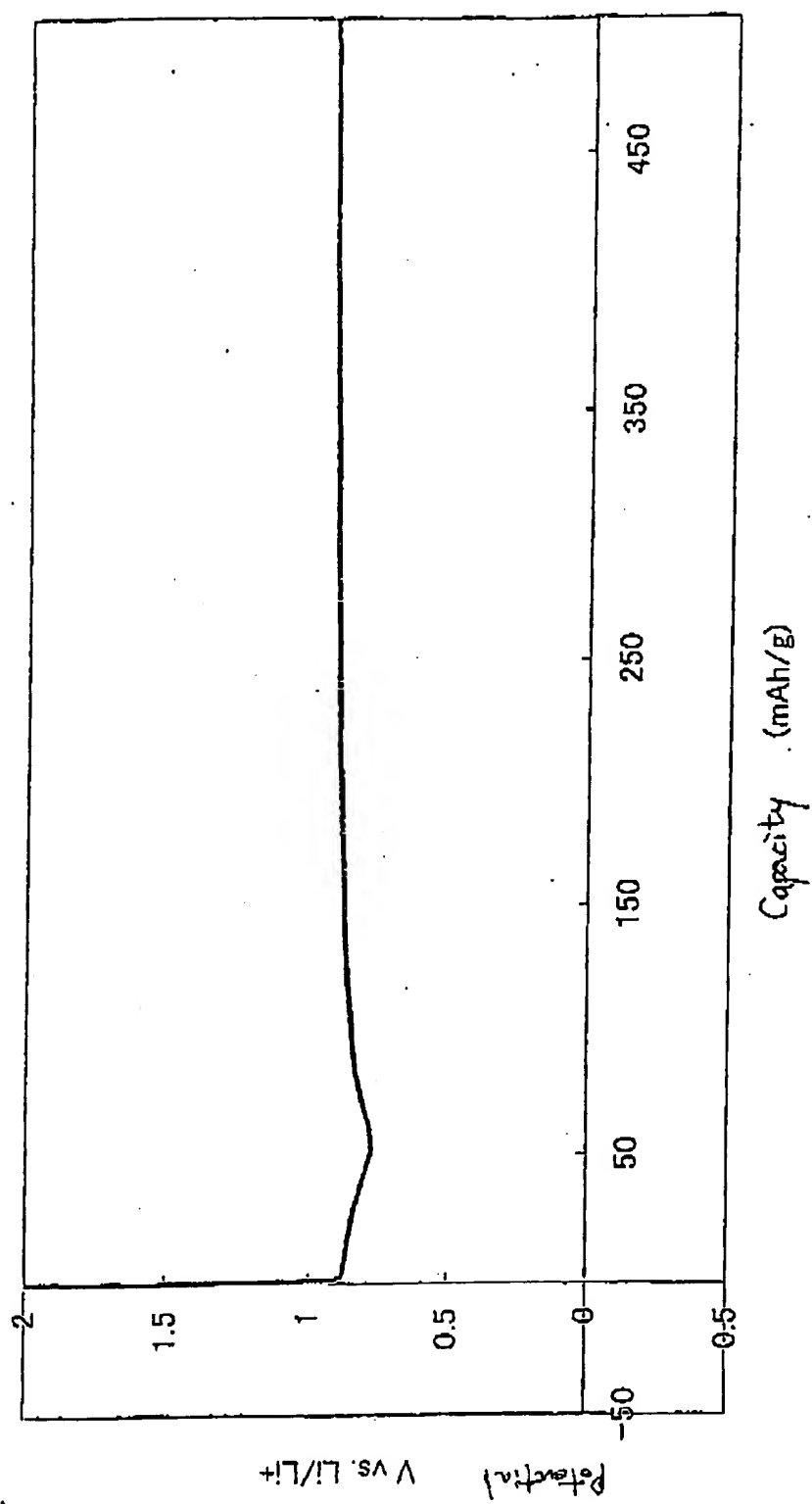
[Fig. 1]



[Fig. 2]



[Fig. 3]



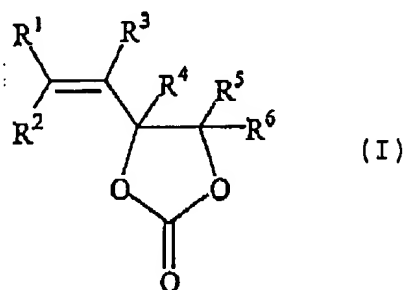
[Designation of Document] Abstract

[Abstract]

[Problem] To provide a battery which is subject to minimized decomposition of the electrolyte and provides a high capacity as well as exhibits excellent storage properties and cycle life performance even at a high temperature.

[Means for Resolution] A non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, characterized in that the foregoing non-aqueous solvent contains a vinyl ethylene carbonate compound represented by the following general formula (I) in an amount of from 0.01% to 20% by weight:

[Ka 1]



wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

[Selected Drawing] none